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## WHAT IS CLAIMED IS:

- A method which comprises electrospinning a pressurized polymer formulation optionally containing an organic solvent into a pressurized collection vessel such that polymer fibers are formed essentially free of said organic optional solvent.
  - 2. The method of claim 1, wherein the pressure in the collection vessel ranges from about 50 psig to about 10,000 psig.
  - 3. The method of claim 2, wherein the pressure ranges from about 50 psig to about 3000 psig.
- 4. The method of claim 1, wherein the temperature in the collection vessel ranges from about 10°C to about 200°C.
  - 5. The method of claim 4, wherein the temperature ranges from about 20°C to about 60°C.
- 6. The method of claim 1, wherein the collection vessel contains a pressurized fluid selected from the group consisting of carbon dioxide, nitrous oxide, alkanes, alkenes, ammonia, ethers, noble gases, SF<sub>6</sub>, water and halogenated hydrocarbons.
- 7. The method of claim 1, wherein the pressure in the collection vessel is less than the pressure applied to the polymer formulation.
- 8. The method of claim 1, wherein the polymer is selected from the group consisting of polyolefins, polyesters, polyamides, polyurethanes, vinyl polymers, elastomers, fluorinated polymers, polyethers, heterocyclic polymers and polyvinyl pyrrolidone or mixture thereof.

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- 9. The method of claim 1, wherein the polymer formulation contains at least one organic solvent and/or contains a pressurized or supercritical fluid.
  - 10. A method of preparing polymeric fibers comprising:
- (a) forming polymeric fibers by electrospinning a liquid polymeric formulation comprising a fiber-forming polymer and an optional organic solvent for the polymer into a collection vessel containing a pressurized fluid;
  - (b) contacting the polymeric fibers with the pressurized fluid in the collection vessel and optionally extracting the organic solvent into the pressurized fluid; and
  - (c) recovering polymeric fibers which are essentially free of said optional organic solvent.
- 11. The method of claim 10, further comprising introducing a pressurized fluid into a mixing vessel containing the polymeric formulation prior to electrospinning the polymeric formulation into the collection vessel, the polymeric formulation comprising a fiber forming polymer and at least one organic solvent or a pure polymer melt.
- 20 12. The method of claim 10, wherein the pressure in the collection vessel ranges from about 50 psig to about 10,000 psig and the temperature in the collection vessel ranges from about 10°C to about 200°C.
- 13. The method of claim 12, wherein the pressure in the collection vessel ranges from about 50 psig to about 3000 psig and the temperature ranges from about 20°C to about 60°C.
  - 14. The method of claim 10, wherein the recovered polymeric fibers are nano-fibers and/or micro-fibers.

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- 15. The method of claim 10, wherein the pressurized fluid is selected from the group consisting of carbon dioxide, nitrous oxide, alkanes, alkenes, ammonia, ethers, noble gases, SF<sub>6</sub>, water and halogenated hydrocarbons.
- 5 16. The method of claim 15, wherein the pressurized fluid is carbon dioxide in a supercritical or a subcritical state.
  - 17. The method of claim 10, wherein the fiber-forming polymer is selected from the group consisting of polyolefins, polyesters, polyamides, polyurethanes, vinyl polymers, elastomers, fluorinated polymers, polyethers, and heterocyclic polymers and polyvinylpyrrolidone or mixture thereof.
    - 18. The method of claim 10, wherein the organic solvent is non-volatile at ambient temperatures and pressures.
    - 19. The method of claim 10, wherein the pressure in the collection vessel is less than a pressure applied to the polymeric formulation to deliver the polymeric formulation into the collection vessel.
- 20. An electrospun polymer fiber essentially free of organic solvent and having an internal cellular structure with a coherent skin that is ruptured along the fiber axis.
- 21. A discontinuous electrospun polymer fiber prepared by the method of claim 10, having an internal pore structure and an external skin.
  - 22. A continuous electrospun polymer fiber prepared by the method of claim 10, having an internal pore structure and an external skin.
- 30 23. An electrospinning apparatus, comprising:a source of a pressurized polymeric formulation;

- a collection vessel which can pressurized by a pressurized fluid supplied to an interior of the collection vessel;
- a flow tube in fluid communication with the source of pressurized polymeric formulation and through which the pressurized polymeric formulation can be delivered into the interior of the collection vessel;
- a target in the collection vessel on which the pressurized polymeric formulation can be electrospun into fibers; and
- a voltage source establishing an electric field between the flow tube and the target.

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- 24. The apparatus of claim 23, further comprising a source of pressurized fluid in fluid communication with the interior of the collection vessel.
- 25. The apparatus of claim 24, wherein the pressurized fluid is a supercritical fluid.
  - 26. The apparatus of claim 23, wherein the interior of the collection vessel contains supercritical carbon dioxide and the source of the pressurized polymeric formulation is a pressurized mixing vessel in fluid communication with the flow tube.
  - 27. The apparatus of claim 23, wherein the source of pressurized polymeric formulation supplies the pressurized polymeric formulation at a constant flow rate to the flow tube.

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- 28. The apparatus of claim 26, wherein the source of pressurized polymeric formulation supplies the polymeric formulation to the flow tube at a pressure at least 5 psi greater than the pressure in the interior of the vessel.
- 30 29. The apparatus of claim 23, wherein the flow tube is electrically grounded and the voltage source comprises an electrically charged electrode in the vicinity of the target.